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## STRUCTURE OF BOROSILICATE GLASS ACCORDING TO RAMAN SPECTROSCOPY DATA

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Glass of the  $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$  system with a  $\text{B}_2\text{O}_3$  content from 20 to 40% was investigated by high-temperature Raman spectroscopy. It was shown that when the boron oxide content was gradually increased, the silicate network undergoes depolymerization, which is confirmed by the change in the ratio of the intensities of the bands characteristic of tetrahedrons with a different number of nonbridge oxygen atoms ( $Q^2$  and  $Q^3$ ). The borate constituent has  $\text{BO}_4$  tetrahedrons which then alternate with nonsymmetrical  $\text{BO}_3$  triangles with nonbridge oxygen atoms.

**Key words:** sodium borosilicate glass, Raman spectroscopy, composition, structure, properties.

Three-component silicate systems that contain another oxide in addition to silicon dioxide — a glass former — are of great interest both from a scientific and a manufacturing point of view. The borosilicate system is one of the most important, and studying it is of enormous importance, particularly for developing glass for different applications and matrices for burial of radioactive wastes. We know [1] that the properties of these matrices are determined to a significant degree by the coordination and structural position of boron in borosilicate glasses. Obtaining information on the structure of the glasses is not only necessary for understanding the nature of the glass state, but also for directed synthesis of materials with defined properties.

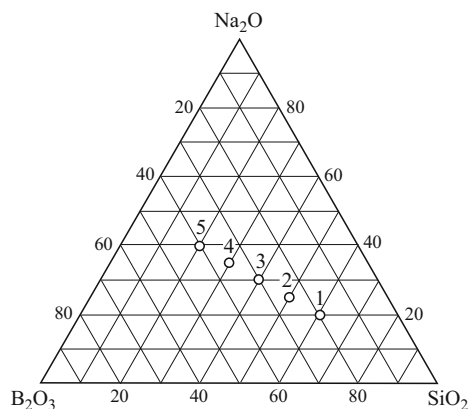
Borosilicate glasses are systems with two cationic glass formers, each of which can form its own anion groups in reacting with alkali metal oxides. The features of formation of borate and silicate constituents and their reaction determine the basic structural features and physicochemical properties of borosilicate glasses and melts. In addition, the properties of borosilicate glasses are a function of the structural state of the boron in the system, which can change its coordination number from three to four as a function of the composition. Varying the concentration of boron in the glasses and changing its coordination allows controlling their properties within wide limits, which is of interest with respect to using them as promising materials in radiation materials science.

Three-component glasses of the  $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$  system were synthesized from analytically pure amorphous

$\text{SiO}_2$ , very pure boron trioxide, and cp carbonate  $\text{Na}_2\text{CO}_3$ . Samples of sodium borosilicate glasses with a  $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$  ratio equal to one and a different  $\text{SiO}_2$  content were investigated (Fig. 1). The batch was carefully mixed in a mortar with alcohol, dried, and melted in a platinum crucible in a Silit furnace at a temperature below 1473 K until the melt was totally homogenized and then air hardened.

The structure of the borosilicate glasses as a function of the composition ( $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$  system with a mass content of  $\text{B}_2\text{O}_3$  of 20 to 40%<sup>3</sup>) was investigated by Raman spectroscopy. A Labram iHR 320 spectrometer with an Olympus BX41 microscope was used for recording the

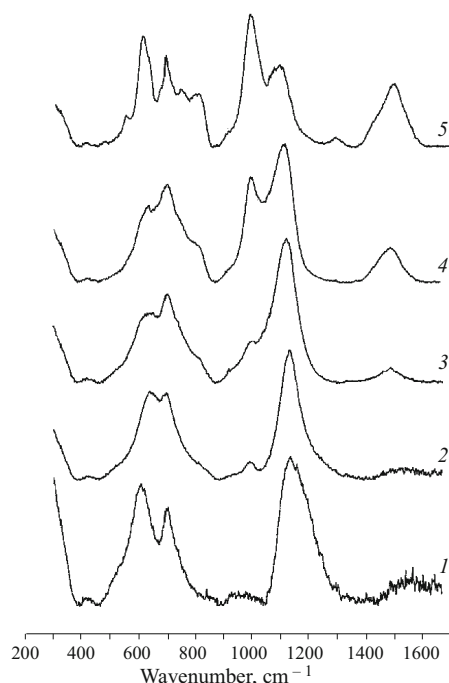
<sup>3</sup> Here and below, mass content.



**Fig. 1.** Composition diagram of the  $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$  three-component system (the numbers of the compositions of the synthesized glasses are designated by the points).

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**Fig. 2.** Raman spectra of glasses of the composition  $x\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (100 - 2x)\text{SiO}_2$ , where  $x(\%) = 20$  (1), 25 (2), 30 (3), 35 (4), 40 (5).

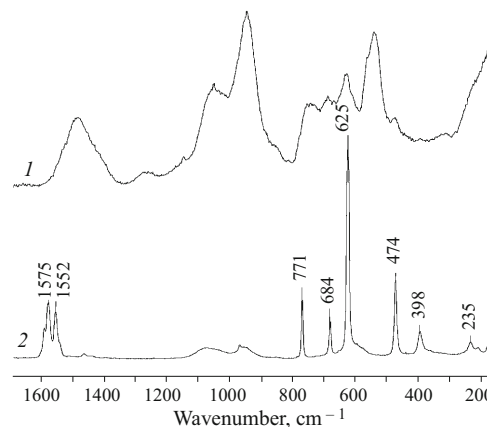
Raman spectra. A base-line correction procedure was run for all of the recorded spectra. The spectra were processed with the OMNIC Thermo Nicolet software package.

The Raman spectra of the investigated glasses obtained at room temperature are shown in Fig. 2.

In analyzing the Raman spectroscopic data for the borosilicate glasses, we can arbitrarily distinguish three regions: 300 – 800, 800 – 1200, and 1200 – 1700  $\text{cm}^{-1}$ . In the region of vibrations of silicate groups (800 – 1200  $\text{cm}^{-1}$ ), the bands are due to stretching vibrations of terminal groups of silicon-oxygen tetrahedrons  $Q^n$  with a different ratio of bridge and nonbridge oxygen atoms ( $n$  is the number of bridge oxygen atoms).

There is one basic band at approximately 1080  $\text{cm}^{-1}$  due to stretching vibrations of nonbridge bonds of  $Q^3$  structural units in the spectrum of glass of the composition 20%  $\text{Na}_2\text{O}$ , 20%  $\text{B}_2\text{O}_3$ , and 60%  $\text{SiO}_2$  in the region of characteristic vibrations of silicate groups. When boron oxide is added, the intensity of this band decreases and the band at 950  $\text{cm}^{-1}$  increases, due to formation of  $Q^2$  structural groups. With a low  $\text{B}_2\text{O}_3$  content, the silicon-oxygen tetrahedrons are primarily joined in layers consisting of  $Q^3$  units. When the boron oxide and sodium oxide content increases, depolymerization of the structure and formation of chain anion groups of  $Q^2$  structural units take place.

In the low-frequency region of the spectrum, the 530  $\text{cm}^{-1}$  band, which is the basic band in glass with 20%  $\text{B}_2\text{O}_3$ , is due to symmetrical stretching and partially deformation vibrations of Si – O – Si bridges [2]. The bands in the



**Fig. 3.** Raman spectra of glass (1) and crystallization products of melt (2) of the composition 40%  $\text{Na}_2\text{O}$ , 40%  $\text{B}_2\text{O}_3$ , and 20%  $\text{SiO}_2$ .

610 – 630  $\text{cm}^{-1}$  region are due to vibrations of metaborate anions of the ring type [3]. On addition of boron oxide, the ratio of the intensities of the 530 and 630  $\text{cm}^{-1}$  bands changes in the low-frequency region of the spectra, which corresponds to an increase in the content of borate groups in the glass. It is interesting that in all five compositions investigated, the 630  $\text{cm}^{-1}$  band is clearly expressed, which indicates the presence of metaborate rings constructed of  $\text{BO}_4$  tetrahedrons. This result is confirmed by the analysis of the Raman spectrum of the crystalline phase obtained in cooling a melt of 40%  $\text{Na}_2\text{O}$ , 40%  $\text{B}_2\text{O}_3$ , and 20%  $\text{SiO}_2$  (Fig. 3). The frequencies of the narrow bands are indicated in the spectrum and we assigned them to vibrations of sodium metaborate, which is in agreement with the data in [4]. The presence of this crystalline compound is also confirmed by the x-ray phase analysis conducted. In addition, the spectrum contains wide bands in the 900 – 1200  $\text{cm}^{-1}$  region, caused by vibrations of an uncrystallized silicate constituent.

There is a new band with a maximum at approximately 770  $\text{cm}^{-1}$  (which is clearly seen) in the glasses with a high  $\text{B}_2\text{O}_3$  content, caused by vibrations of four-coordination boron [5].

There is a complex band with a maximum at 1490  $\text{cm}^{-1}$  which is basically due to vibrations of  $\text{BO}_3$  triangles with one nonbridge oxygen atom in the region of vibrations of borate groups [3]. The intensity of this band and consequently the content of these structural units increase with an increase in the  $\text{B}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  content in the glass. In addition, a new band appears in the 1266  $\text{cm}^{-1}$  region caused by stretching vibrations of B – O bonds in borate triangles appears in the spectrum of glass of the composition 40%  $\text{Na}_2\text{O}$ , 40%  $\text{B}_2\text{O}_3$ , and 20%  $\text{SiO}_2$ .

Raman spectroscopy thus showed that significant structural changes take place in the  $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$  system with a gradual increase in the boron oxide and sodium oxide content when the ratio of  $\text{Na}_2\text{O} : \text{B}_2\text{O}_3 = 1$  is respected. The silicate network undergoes depolymerization, confirmed by the change in the ratio of the intensities of the bands charac-

teristic of tetrahedrons with a different number of nonbridge oxygen atoms ( $Q^2$  and  $Q^3$ ).  $BO_4$  tetrahedrons are present in the borate constituent and then are replaced by nonsymmetrical  $BO_3$  triangles with nonbridge oxygen atoms.

The studies showed that glasses of the  $Na_2O - B_2O_3 - SiO_2$  system with a  $B_2O_3$  content of 20 to 40% can be used in radiation materials science.

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